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CARBON FIBRE ELECTROCHEMICAL DETECTOR FOR HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

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SUMMARY

A voltammetric detector has been designed, based on a strand of glassy carbon fibres placed in a plastic capillary connected to the column outlet. The eluate leaves the capillary through a hole in the wall. The capillary is immersed in a macroscopic vessel containing the mobile phase and a reference and counter electrodes. The detector is extremely simple, cheap and reliable in operation. It is easy to attain a very small working volume. The detector performance was tested with adrenaline. Its operating parameters are fully comparable with those of classical thin-layer and wall-jet detectors and it is very sensitive (typical detection limit for adrenaline, 20 pg).

INTRODUCTION

Recently, electrochemical detection (ED) techniques have found extensive use in high-performance liquid chromatography (HPLC) (for a survey see, *e.g.*, ref. 1). Among voltammetric detectors with solid electrodes, the thin-layer and wall-jet types are by far the most common. These detectors are reliable, but require careful manufacture and maintenance, especially if very small cell volumes are to be attained.

In the present paper we describe a very simple detector using glassy carbon fibres that removes these difficulties. So far, there has been only one report² where a similar principle was used, based on a gold wire placed in a dialysis membrane tube through which the eluate flows. The tube is immersed in a macroscopic vessel containing a base electrolyte with a reference and an auxiliary electrode. This detector has quite a substantial working volume and the separation of the working electrode from the auxiliary and reference electrodes by the membrane may sometimes cause difficulties in the control of the working electrode potential.

EXPERIMENTAL

Detector design

The detector is depicted in Fig. 1. The working electrode consists of a strand of glassy carbon fibres, diameter 4–7 μm (Monokrystaly, Turnov, Czechoslovakia) placed in a PTFE tube (0.6 mm I.D.). One end of the tube is connected to the column outlet. The working length of the detector is defined by the length of the fibres to the hole in the wall of the tube through which the eluate leaves. A silicone rubber seal prevents the penetration of the eluate beyond the hole. A copper wire is inserted into the other end of the tube and a good electrical contact with the fibres is achieved by placing a stainless-steel clip tightly around the tube. The tube is placed in an overflow vessel containing a base electrolyte (the mobile phase) and an auxiliary and a reference electrode are placed close to the eluate outlet.

A disadvantage of this arrangement is the fact that the hydrodynamics of the working electrode may change by accidentally changing the position of the PTFE tube. For this reason, and in view of the intended use of this detector with microbore columns, the design was somewhat modified (Fig. 2). Here the plastic tube with the carbon fibres is fixed in a detector body which is screwed onto the column outlet. The tube passes through a drilled glass frit onto which a reference electrode is pressed. A stainless-steel outlet tube serves as the auxiliary electrode. The results presented in this paper were obtained with the detector depicted in Fig. 1.

Instrumentation and chemicals

The measurements were performed with an LC-XP liquid chromatograph (Pye Unicam, U.K.), using a stainless-steel capillary (80 cm \times 0.2 mm I.D.) to simulate the column. For the determination of the response times and volumes, samples were injected into the detector through a shorter stainless-steel capillary (5 cm \times 0.2 mm I.D.) using either a 20- μl loop or directly through a septum by a syringe (1–10 μl).

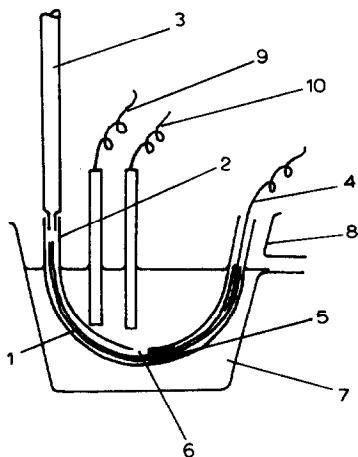


Fig. 1. Carbon fibre detector. 1 = Working electrode (a strand of carbon fibres); 2 = PTFE tube (I.D. 0.6 mm); 3 = column; 4 = electrical contact; 5 = silicone rubber seal; 6 = outlet; 7 = base electrolyte; 8 = overflow vessel; 9 = auxiliary electrode; 10 = reference electrode.

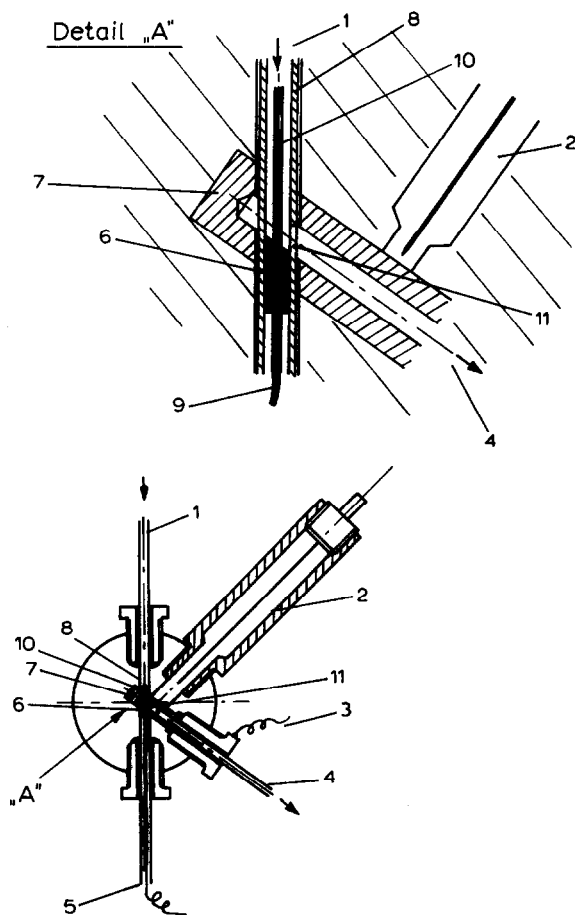


Fig. 2. Modified version of the detector. 1 = Inlet; 2 = reference electrode; 3 = auxiliary electrode; 4 = outlet; 5 = working electrode; 6 = silicone rubber seal; 7 = glass frit; 8 = PTFE tube; 9 = electrical contact; 10 = carbon fibres; 11 = opening.

The detector was operated by an EDLC instrument (Laboratorní Přístroje, Czechoslovakia) permitting the potentiostatic control of the system with noise damping and effective offsetting of the background current, using a saturated Ag/AgCl reference and a platinum auxiliary electrode. A TZ 4200 line recorder (Laboratorní Přístroje) was used.

Adrenaline hydrogen tartrate (Fluka, Buchs, Switzerland) was used as the test compound, in a mobile phase of 60% methanol, 1.8% acetic acid and water containing 0.5 g sodium sulphate per litre.

All measurements were carried out at a working electrode potential of +0.8 V (Ag/AgCl electrode) at room temperature.

RESULTS AND DISCUSSION

The operating parameters of the detector (parameters of the calibration curve,

noise, detection limit, linear dynamic range, response time and volume, precision of measurement and long-term stability of the detector signal) were studied at various mobile phase flow-rates and working lengths of the detector.

The detector geometric volumes were determined as the volumes of distilled water required to fill the working space. The response times were then determined as the times required to attain a current of $I = 0.632 I_{\max}$ upon a step change in the adrenaline concentration, and the response volumes were obtained by multiplying the response times by the flow-rate³. These results are summarized in Table I.

From the values in Table I, as expected, the shortest possible detector should be used from the point of view of the response time and volume. A very short working length is also advantageous because the potential distribution along the working electrode is more homogeneous than with long fibres (shorter distance from the auxiliary and reference electrodes). The dependences of these values on the mobile phase flow-rate was less pronounced than observed earlier³. The response volumes are not much larger than the geometrical volumes, indicating that the detector behaves as a good mixing chamber. For use with microbore columns it will be necessary to decrease further the geometric volume, by using narrower tubing. However, no excessive peak broadening or tailing was observed on increasing the detector length from 8 to 82 mm under the present conditions.

The noise value is virtually independent of the detector length and the mobile phase flow-rate and varies from $2 \cdot 10^{-11}$ to $8 \cdot 10^{-11}$ A. The parameters of the calibration curve are similar for all the detector lengths tested, typical values being: slope, 3.73 nA/ng; correlation coefficient, 0.9967 (for a detector 8 mm long at a flow-rate of 0.2 ml/min). Under these conditions, the detection limit, calculated as twice the absolute noise value, is 20 pg adrenaline. The detector is thus highly sensitive. The linearity of the calibration curve (peak heights) is satisfactory, but the linear dynamic range is somewhat narrower than with thin-layer and wall-jet detectors studied previously⁴; at adrenaline amounts higher than *ca.* 50 ng the calibration curve ceases to be linear (the slope decreases). Therefore, it seems that the detector will be most useful for trace analysis. However, the calibration curve is linear down to the lowest detectable amount, *i.e.*, 20 pg.

TABLE I

DEPENDENCES OF THE GEOMETRIC VOLUME, RESPONSE TIME AND RESPONSE VOLUME ON THE DETECTOR WORKING LENGTH

Detector length (mm)	Geometric volume (μ l)	Flow-rate (ml/min)					
		0.1		0.2		0.3	
		Response time (sec)	Response volume (μ l)	Response time (sec)	Response volume (μ l)	Response time (sec)	Response volume (μ l)
82	12.0	11.1	18.5	5.6	18.7	4.0	20.2
76	7.0	7.6	13.0	4.9	16.2	3.3	16.4
61	5.8	5.8	9.7	3.6	12.2	2.5	12.6
15	1.5	1.5	2.6	1.0	3.3	0.6	3.2
8	0.4	0.4	0.7	0.3	1.0	0.2	1.0

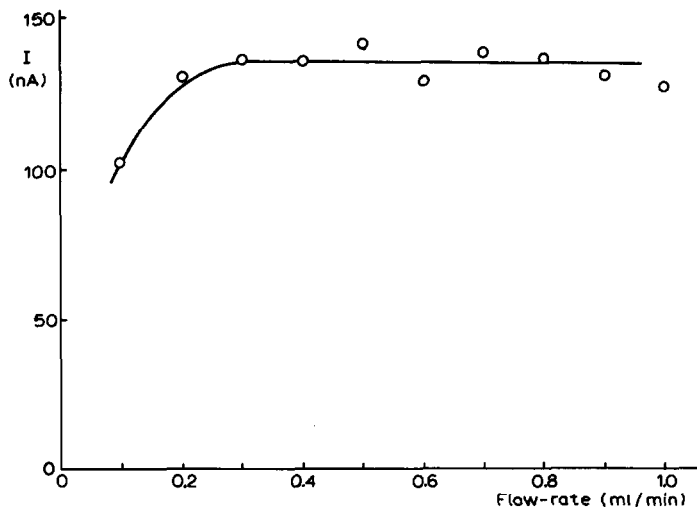


Fig. 3. Dependence of the detector signal on the mobile phase flow-rate (35 ng adrenaline).

As the active surface area of the working electrode is quite large with carbon fibres, we tested the possibility of using it in the coulometric mode. We calculated the theoretical charge required to oxidize the adrenaline amount injected and compared it with the area under the recorded peak. However, the degree of conversion is low, namely, 0.44% for a flow-rate of 0.2 ml/min and 2.8% for a flow-rate of 0.1 ml/min (detector working length, 82 mm). Hence, it seems that coulometry could only be used at extremely low mobile phase flow-rates.

The dependence of the detector signal on the mobile phase flow-rate, measured within the range 0.1–1.0 ml/min, is much less pronounced than with other voltammetric detectors (see Fig. 3). There is an increase in the signal with increasing flow-rate only at the lowest flow-rates and then the signal is virtually independent of flow-rate. This will be an advantage when working at optimum flow-rates in HPLC.

A great problem in working with solid electrodes is the electrode passivation, causing long-time irreproducibility of the signal. In the present detector, the working electrode cannot be reactivated mechanically, only by chemical and electrochemical means. However, no electrode passivation was observed during the time of the experiments, *i.e.*, for about 3 months. However, even if the working electrode became passive, it can readily be replaced, as it is very cheap and easy to manufacture.

The reproducibility of measurement is similar to that obtained with other types of voltammetric detectors. Typical values of the relative standard deviation (five parallel measurements, $\alpha = 0.05$) are 2.7% for adrenaline amounts greater than 50 ng, 4.7% for amounts around 1 ng and about 10% for amounts less than 0.1 ng.

CONCLUSIONS

The described detector is very cheap, easy to prepare and very reliable. It is highly sensitive and exhibits a good linearity at low solute concentrations, but its linear dynamic range is limited at higher solute concentrations. It is promising for

use in trace analysis and in combination with microbore columns. Its hydrodynamics cannot be exactly described, but they will be constant provided that the shape of the working part is maintained constant. The operating parameters of the detector are similar to those of other solid electrode detectors, and the small signal dependence on the flow-rate is advantageous when working at flow-rates greater than *ca.* 0.2 ml/min.

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